

Direct Methanol Fuel Cells - Progress, Problems and Prospects

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Introduction

In spite of the substantial technological advances made in the area of rechargeable lithium-ion batteries, the need for high energy density portable power sources continues to grow in the civilian and military sector. This need for high energy density power sources is driven by the increased energy usage by multifunctional electronic equipment, the decreasing size of portable electronic equipment, and the need for operating continuously without interruptions for re-charging. Thus, portable fuel cell technologies based on high energy fuels such as methanol continue to be extremely attractive. The inherent high energy density of methanol as a fuel presents the potential of a ten-fold increase in specific energy over the state-of-art lithium ion batteries. In addition, the possibility of instant re-fueling with a fresh fuel cartridge mitigates the inconvenience of battery re-charging arising from downtime, the need to be close to source of primary power, and the mass and volume penalty associated with additional batteries and recharging equipment. As a result, there has been considerable effort in the last 15 years to advance the technology of methanol-based portable fuel cells. This paper attempts to survey the progress, problems and prospects of realizing the advantages of portable power sources based on the direct methanol fuel cell (DMFC) technology.

Features and Advantages of Direct Methanol Fuel Cell Technology

The direct methanol fuel cell is based on the direct electro-oxidation of an aqueous solution of methanol in a polymer electrolyte membrane fuel cell without the use of a fuel processor. With the direct methanol fuel cell system the complexity of processing the methanol into hydrogen is eliminated. The liquid feed operation also facilitates instant start-up and easy thermal management of the stack. Membrane electrode assemblies for methanol - air fuel cells are fabricated by bonding catalyzed electrodes to either side of a proton conducting membrane similar to hydrogen-air fuel cells. Platinum-ruthenium alloy is the preferred catalyst for methanol oxidation and platinum is used for oxygen reduction. The important characteristics of this fuel cell have been discussed in earlier papers by the authors and other groups [1-7]. The theoretical energy content of methanol is approximately 6000 Wh/kg. Hydrogen storage systems even with 10 % storage (by weight) can only offer a theoretical energy content of 3200 Wh/kg. Also, the goal of 10% for hydrogen storage is still far from being demonstrated, with state-of-art systems featuring about 1.5-2 wt% storage. Methanol, being a liquid fuel, can be transported at ambient pressures as a pure liquid or as an aqueous solution. Several permissions have now been granted for transport of methanol on passenger aircraft. Thus, methanol can be deployed in a consumer environment with relatively lower concern compared to hydrogen, and portable power systems that can be refueled by the consumer from a

disposable cartridge or fuel bag are conceivable. Methanol fuel cells have demonstrated fuel-to-electric efficiencies in the range of 25-30% and this is about 50% of what can be realized with hydrogen-air fuel cells. However, in spite of the lower efficiencies of the direct methanol fuel cell, this fuel cell system with its compact fuel storage can compete in mass and volume with state-of-art hydrogen-air systems. Also, the technological advances in performance and efficiency of direct methanol fuel cells achieved in the last ten years have led to the design of several prototype demonstration units by various organizations. These system demonstrations to date have focused on proving the feasibility of novel stack designs, new membrane types, integrated system configurations, scale-up, fuel delivery methods, and miniaturization concepts. Systems are now available commercially for battery recharging applications at least from one manufacturer.

Membrane Electrode Assemblies

The performance of the direct methanol fuel cell depends on the characteristics of the membrane-electrode assemblies. The membrane-electrode assemblies are constructed from a proton exchange membrane such as Nafion 117 (Du Pont) on to which catalyst layers consisting of noble metal catalysts are applied. Platinum-ruthenium (1:1, Johnson-Matthey High Spec 6000) is a widely-used catalyst for the oxidation of methanol, and platinum-black (Johnson Matthey, fuel cell grade) is a commonly-used catalyst for the cathode. Catalyst loading levels as high as 8 mg/cm^2 are used on each electrode to achieve high performance. For a viable system design that maintains thermal and water balance, the performance of the cell at 60°C at low flow rates of air is very important. Performance at low air flow rates is limited by the demands for air from methanol crossing over to the cathode, the carbon dioxide blanket created by the crossover reaction and the large quantities of liquid water that are drawn across the cell by the electro-osmotic transport process. To overcome these limitations, MEAs are usually operated at three to four times the stoichiometric flow rates. This limits the system design from not being able to operate in environments that are hotter than 40°C . Military applications require the capability to operate at temperatures as hot as 50°C . Figure 1 shows the significant improvements in performance at low air flow rates have been achieved through improvements to the cathode structure. With this type of advanced MEA, fairly compact systems can be built and operated up to an environmental temperature of 48°C . Even with these improvements, the need to operate at flow rates of less than two times the stoichiometric requirement entails significant polarization losses at the cathode at current densities greater than 100 mA/cm^2 . Further improvements to the cathode can benefit from a membrane with low methanol crossover such as the one developed by USC and JPL[8]. More recently, Du Pont has also reported improved performance with lower crossover membranes developed specifically for DMFC [9]. Cells operating on natural air convection are inherently limited to operation at extremely low power density because of the mass transfer barriers.

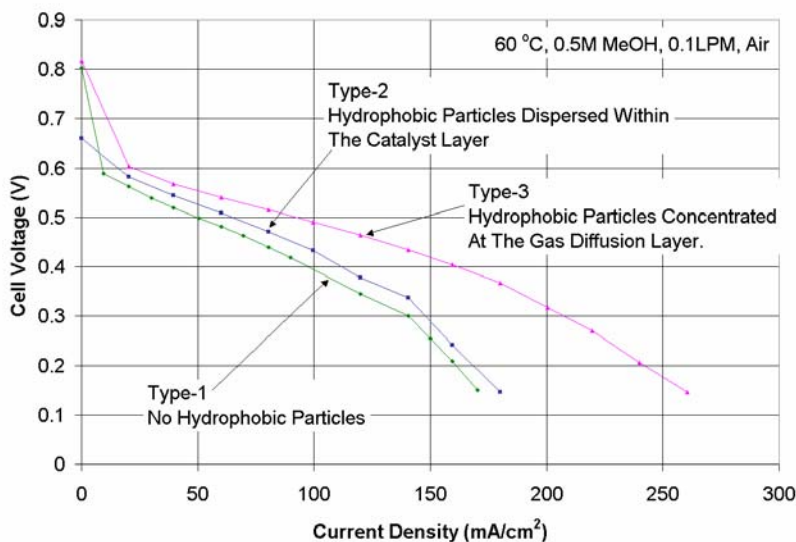


Figure 1. Performance of advanced MEA with improved cathode structure for direct methanol fuel cell based on Nafion 117.

One of the key issues limiting the large-scale deployment of the direct methanol fuel cell is the cost of catalyst. Lowering the amount of noble metal used in the catalyst layer from its current value at 4-8 mg/cm² will substantially reduce the cost of the cells. JPL has recently prepared and demonstrated MEAs that perform at ultra-low catalyst loadings. These catalyst layers were applied by the sputter deposition technique. Results of MEAs with catalyst loadings of 0.1 mg/cm² are shown in Figure 2.

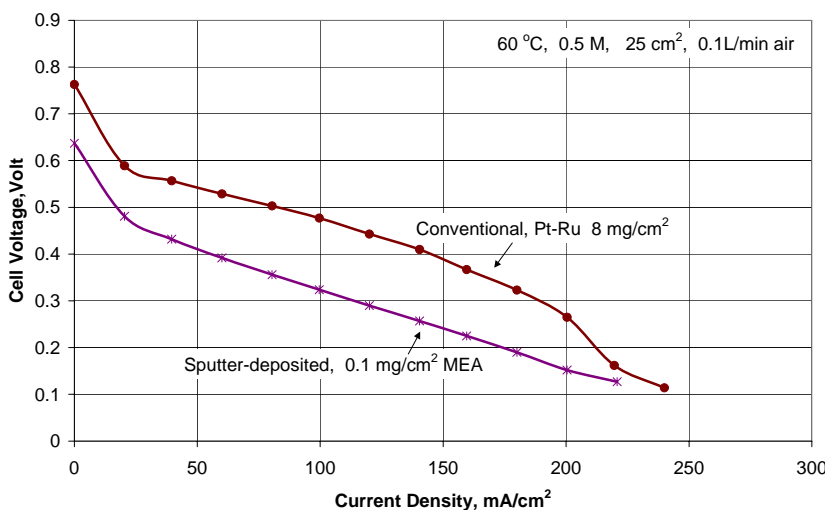


Figure 2. Comparison of the performance of an MEA with a sputter deposited Pt-Ru catalyst layer (0.1 mg/cm²) with a conventionally prepared MEA with Pt-Ru black catalyst (8 mg/cm²).

In order to further improve the activity of the anode catalysts, JPL is pursuing a combinatorial catalyst discovery approach using sputter deposition of catalyst layers. Thus, new non-noble metal containing nickel and zirconium compositions have been identified using the rapid and robust combinatorial screening methodology described in a

recent publication [10]. Importantly, these non-noble metal catalysts do not corrode in acidic media and can also be prepared as thin film sputtered layers or even as powder materials. Analyses on this material showed that the nickel and zirconium rich compositions were nanophase/amorphous in structure and possessed a very different electronic structure from that of the common fcc Pt-based alloys usually used for DMFC anode catalysis. Results in Figure 3 show that the performance of the non-noble metal compositions is comparable with that of platinum-ruthenium, suggesting that this is a promising avenue for further optimization.

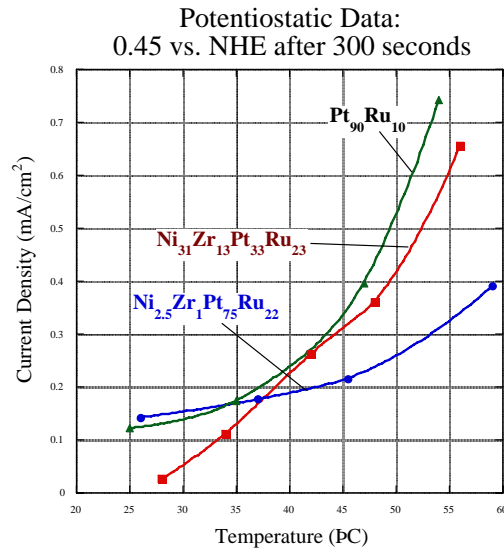


Figure 3. Performance of nickel-zirconium based catalysts for methanol oxidation.

More recently, the stability of commercial platinum-ruthenium catalysts has become a serious cause for concern. Recent studies from the Los Alamos National Laboratory have shown that ruthenium dissolves from the platinum-ruthenium catalysts [11] even during normal operation. The ruthenium that dissolves from the anode crosses over to the cathode and reduces the cell performance. Studies at JPL have confirmed that the durability of MEAs are definitely compromised by the dissolution of ruthenium from the anode. Based on the electrochemistry of ruthenium and the Pourbaix diagrams, by restricting the anode potential below 0.8V vs. NHE, ruthenium dissolution should not occur. However, recent results seem to contradict this hypothesis. More work is needed to understand this problem, as it is fundamental to the durability of the MEAs.

Stacks and Systems

Over the last five years, conventional bipolar stack designs have been demonstrated by various organizations. These stacks consist of 10 or more cells and active areas ranging from 20 to 200 cm² and power ranges from 10 -1500 Watts. The power density of these stacks is in the range of 15-20 W/kg when examined under operating conditions that allow a system to be designed and operated. The need for increasing the power density of stacks has prompted the development of lightweight stack designs. The weight of the bipolar plates and endplates in a bipolar stack is usually 80-90% of the stack mass in conventional stacks. Bipolar plates are crucial in minimizing voltage losses when operating at

high stack currents. However, when the actual currents flowing through the stack are small, higher cell impedance configurations may be acceptable. This would be an attractive especially if significant weight reduction can be accomplished with an acceptable stack impedance. Such a compromise is readily achieved in monopolar configurations where the current is collected along the edges, or in the plane of the electrodes and bipolar plates are eliminated. Challenges of designing monopolar stacks rest in minimizing orientation insensitivity, water removal and achieving good sealing. An example of a monopolar stack that can provide 50 Watts/kg operating at 35°C have been developed at the Jet Propulsion Laboratory, and have been demonstrated in a 5 – Watt unit shown in Figure 4. Such monopolar stack designs can potentially achieve 120 W/kg when operating at 60°C, and this would result in doubling of the state-of-art performance.

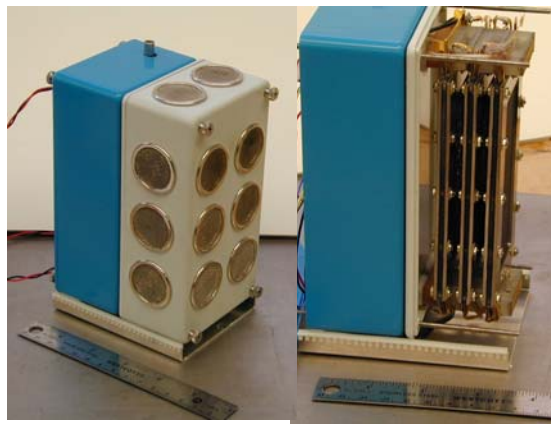


Figure 4. A 5-watt system assembled with a lightweight monopolar stack

A 50 Watt DMFC system is now available commercially from Smart Fuel Cells Inc. This unit is designed for charging lead acid batteries in recreational vehicles. A photograph of such a system is shown in Figure 5. JPL is currently evaluating the performance of these systems. Initial results suggest that the product is well-suited for the specific application. Smart Fuel Cells continues to address the need for small fuel cell systems at the 20-25 Watt level.



Figure 5. 50-Watt DMFC system manufactured by Smart Fuel Cell Inc.

Recently, JPL designed, fabricated and tested a 300-Watt DMFC unit for military applications. A photograph of this unit showing the internal components is shown in Figure 6.

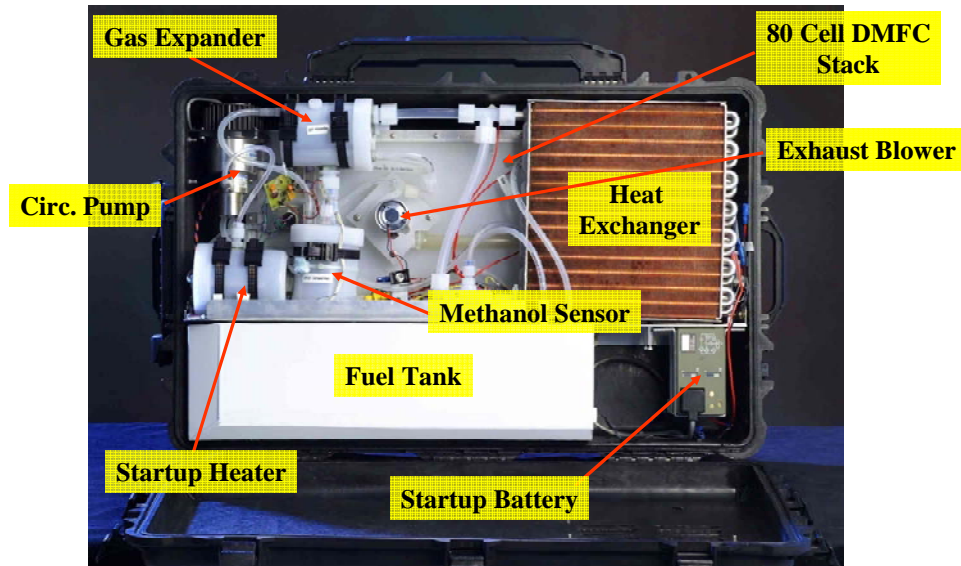


Figure 6. 300-Watt/30,000 Wh system designed and demonstrated at JPL

This system was designed to provide 30,000 Wh of electricity and an energy density of greater than 540 Wh/kg including the fuel storage. The system consisted of an in-house fabricated 80-cell stack (electrode active area of 80 cm², Nafion-117, external air manifold bipolar design), methanol sensor, features for instant start-up and variable load handling. The autonomous operation of this system was demonstrated in a laboratory environment. The stack performance in this unit declined substantially over a period of six months. Investigations revealed that “overdischarge” of the cells sustained by the shunt currents in the stack caused the ruthenium to dissolve from the anode and deposit at the cathode leading to 50% reduction in performance. Thus, shunt currents were important to consider in the operation of liquid and electrolyte fed fuel cells. These studies on the 300-Watt system highlight some of key issues with operating a multi-cell liquid-fed stack and the limitations of an externally manifolded stack design in not being able to regulate the oxidant availability following shut down. These limitations can be overcome with internally manifolded stacks although the parasitic power loss resulting from pressure drops will be slightly higher.

Since methanol fuel cell systems can be controlled readily under a steady state load, the future will also see movement of system designs to incorporate a hybrid lithium-ion battery for handling variable loads. This will enlarge the range of loads the systems can handle and also improve the efficiency of the system. The size of conventionally designed methanol fuel cell systems can be reduced if the demand for liquid recirculation on the anode side and liquid water recovery from the cathode side can be eliminated. This will depend on new concepts that will allow the methanol to be completely oxidized in a single pass and also internal water return through the membrane. Such systems when combined with lightweight stacks deployed with high activity MEAs,

will result in as much as 50% reduction in the size and 75% reduction in mass of direct methanol fuel cell systems.

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References:

1. S.Surampudi, S. R. Narayanan, E. Vamos, H. Frank and G.Halpert, A. Laconti, J. Kosek, G. K. Surya Prakash, and G. A. Olah, *J. Power Sources*, **47**, 377 (1994).
2. S. R. Narayanan, A. Kindler, B. Jeffries-Nakamura, W. Chun, H. Frank, M.Smart , S. Surampudi and G. Halpert, in “*Proton Conducting Fuel Cells I*”, S. Gottesfeld, G. Halpert and A. Landgrebe, Editors, PV 95-23, p.261 The Electrochemical Society, Proceedings Series, Pennington, NJ (1995).
3. X. Ren, M. S. Wilson, and S. Gottesfeld, *J. Electrochem. Soc.*, **143** L12 (1996).
4. S. R. Narayanan, T. Valdez, N. Rohatgi, J. Christiansen, W.Chun, G. Voecks and G. Halpert, Proceedings of the 38th Power Sources Conference, p. 461, Cherry Hill, NJ, 1998.
5. S. R. Narayanan, T. I. Valdez, N. Rohatgi, W.Chun and G. Halpert, *1998 Fuel Cell Seminar*, Abstracts, p. 707, Palm Springs, CA November 1998.
6. T. I. Valdez and S. R. Narayanan, “*Proton Conducting Fuel Cells II*”, S. Gottesfeld, and T. Fuller, Editors, PV 98-27, p. 380 The Electrochemical Society, Proceedings Series, Pennington, NJ (1998).
7. P. Zelenay, S.C. Thomas and S.Gottesfeld “*Proton Conducting Fuel Cells II*”, S. Gottesfeld, and T. Fuller, Editors, PV 98-27, p. 300 The Electrochemical Society, Proceedings Series, Pennington (1998)
8. G.K.S. Prakash, M. C.Smart , Q.J. Wang, A. Atti , V. Pleyne V, B. Yang, K. McGrath, G. A. Olah, S. R. Narayanan, W. Chun, T. Valdez , S. Surampudi , *J. Fluorine Chemistry*, 125 1217-1230 (2004).
9. M. Abdou, Presentation at Fuel Cell Seminar 2004 Palm Springs,
10. J. Whitacre, T. I. Valdez and S.R. Narayanan, *J. Electrochem.Soc.*, 152 A1780-A1789 (2005).
11. P. Piela, C. Eickes, E. Broscha, F. Garzon and P. Zelenay, *J. Electrochemical Soc.* 151 (12) A2053-A2059, 2004